

Article

Research of the Process of Purification of Sulfate Zinc Solution from Iron Ions Using Anodic Oxidation

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Abstract: The possibility of using a membrane electrolytic cell for the electrochemical oxidation of Fe(II) and purification from impurities of real industrial solutions obtained by atmospheric leaching of low-grade zinc concentrates is considered. The average indicators for carrying out the electrooxidation process are given. The principal possibility of conditioning a zinc sulfate solution by hydrolytic purification with preliminary oxidation of iron in a membrane electrolytic cell with an anion-exchange membrane MA-41 TU 2255-062-05761695-2009 is considered. Carrying out direct electrooxidation of iron (II) in sulfate zinc solutions in the anode chamber of a flow membrane electrolyzer ensures good filterability of precipitates after hydrolytic precipitation of iron, since this solution does not contain Fe(II) ions, the presence of which leads to significant difficulties in the operations of separating solid and liquid phases. This makes it possible to exclude the thickening operation from the technological scheme. The degree of oxidation of iron during the test period was 99.8–99.9%. The residual concentration of iron after precipitation from solutions obtained after electrochemical oxidation in the form of oxide and hydroxide compounds was less than 0.01 g/dm³.

Keywords: anion exchange membrane; electrooxidation; iron removal; strongly acidic anion exchanger; sulfate zinc solution



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1. Introduction

Recently, due to the deterioration of the material composition of ores, the content of some impurities that are undesirable for the final target product has increased so much that traditional technological methods either do not provide the necessary purification or significantly increase the cost of the product. It can be noted that around the world, in particular in East Kazakhstan, there is a depletion of reserves of developed deposits of lead-zinc ores [1], as well as a decrease in the quality of the initial zinc raw materials with an increase in the proportion of impurities. This leads to further deterioration of technological performance, which requires deep purification of productive solutions.

In connection with the foregoing, an urgent task of the complex processing of solutions with a high zinc content for the subsequent production of high-quality cathode metal is the separation of impurities, primarily iron, the concentration of which can reach 30 g/dm³.

Iron is usually present in sulfate zinc solutions, in the form of Fe₂(SO₄)₃ [2], removed by the hydrolytic method, and FeSO₄ which does not undergo hydrolysis under neutral leaching conditions [3]. Therefore, to purify this solution, it is necessary to oxidize all the iron in the solution to the trivalent form. The most widespread and cheap way of its oxidation is the use of inorganic substances (hydrogen peroxide, lead dioxide, manganese dioxide, air oxygen, potassium permanganate) [4].

Niu et al., proposed a new method to prevent the formation of harmful iron removal residues [5]. The test results showed that iron hydroxide precipitated in the form of a thin layer of sedimentation at temperatures above 60 °C. During the hydrothermal treatment of the sedimentary layer, the high temperature of the hydrothermal reaction contributed to the complete conversion of iron hydroxide to hematite. The disadvantage of this method is the constant control of the temperature of the hydrothermal reaction and the acidity of the iron-containing solution of zinc sulfate.

In Ref. [6], oxidation by air takes place in sumps to maintain low iron (III) concentrations. To compensate the resulting acid, calcined cinder is continuously added to achieve the preferred pH of 3.5 to 4.0. The required precipitation temperature is about 95 °C.

Fu et al., carried out studies with a microbubble generator with a Venturi jet, which was used to produce oxygen microbubbles [7]. It has been found that the high jet power and high temperature (90 °C) can accelerate the rate of oxidation of Fe²⁺ ions by microbubbles.

The currently widely used methods of oxygen–air and reagent oxidation [8] followed by hydrolytic precipitation of iron [9,10] have several disadvantages:

- long duration of the oxidation process;
- the use of relatively expensive oxidizers;
- loss of non-ferrous metals with cakes and the need for their processing;
- multi-stage cleaning processes.

The reasons for this are the high concentration of iron, the coprecipitation of other valuable components of the solution. Particularly complicating the purification process is the separation of the solid phase during filtration of the resulting hydroxide pulp. There are a number of works aimed at finding optimal solutions in this area in various ways.

In [11], the traditional methods of cleaning the solution from iron are analyzed, and the possibilities of the autoclave method of cleaning the solutions from impurities are considered. As a result of using the autoclave method, 87–89% of the iron can be removed from the solution as hematite.

The use of autoclave equipment for deferrization of sulfate zinc solutions obtained after the zinc cinder leaching stage made it possible to reduce the iron concentration to 1–2 mg/L, while 83.5% of Zn and 52.1% of Cu are extracted from the zinc cinder into the solution. All experiments were carried out with a model solution of the following composition, g/L: H₂SO₄—10–33; Cu—1.5; Mn—5.0; Zn—110; Fe—2.5. Neutralization and purification of the solution was carried out at low-temperature auto-leaching of zinc cinder. The optimal conditions for the precipitation of iron from the zinc solution are as follows: the molar consumption of Zn/H₂SO₄ = 1.3; T = 80 °C t = 1 h; P_{O₂} = 0.2 MPa [12].

Qin et al., studied the behavior of iron in the process of autoclave leaching of zinc sulfide [13]. The behavior of both Zn and Fe during pressure leaching was investigated with changes in temperature, acid addition and leaching time. It was found that the extraction of iron changed with increasing temperature, acidity and leaching time. The authors calculated the degree of dissolution of iron-containing minerals and the degree of precipitation of Fe(III) ions during leaching.

Wang et al., studied the behavior of zinc and iron in the neutralized residue during autoclave leaching with changes in temperature, acidity, leaching time, and oxygen partial pressure [14]. Iron recovery increased with temperature and then decreased with leaching time. It has been established that a high initial acidity is necessary for the decomposition of ferrite in the neutralized residue.

In the next work, the precipitation of iron is carried out with the addition of lime to increase the pH value from about 2 to 4–4.5 within 2 h at 50 °C. After the precipitation of iron, the primary recovery of zinc by extraction was carried out. After extraction, a solution containing 16.6 g/L of Zn; 0.05 g/L of Fe and 0.11 g/L of Mn was subjected to electrolysis [15]. Traditional methods usually use roasting and calcination at this stage, which solves the environmental problem caused by the storage of a large amount of zinc leaching residues [16].

However, these methods do not provide complete removal of iron, and effective purification of solutions from iron is possible by the hydrolytic method, if the maximum amount of dissolved iron is converted into the trivalent form Fe(III).

There are a number of works on the electrochemical purification of zinc solutions. When studying the kinetics of iron oxidation on platinum electrodes coated with Nafion R [17,18], it was found that platinum electrodes coated with this film were particularly effective in reducing the effect of impurities on Fe²⁺ oxidation kinetics. Analyzing the experimental data on electrochemical cleaning, we can say that they were obtained mainly for specific technological solutions. There are practically no studies on the kinetics of the anodic oxidation of Fe(II) to Fe(III).

The reduction of pickling solutions [19–21] by electrochemical oxidation of iron using an electrochemical reactor with a three-dimensional graphite-containing anode was studied. An anion selective membrane was used as a separator to prevent the Fe reduction at the cathode. Complete oxidation of Fe with high current efficiency was found. The method of membrane electrolysis is based on the phenomenon of ion transfer through ion-exchange membranes under the action of an electric current. Ion-exchange membranes differ from porous partitions traditionally used in electrochemistry in that they provide preferential transfer of precisely charged ions. Only cations are transferred through an ideal cation-exchange membrane, and only anions through an anion-exchange membrane [22–24]. The both surfaces of the membrane can be subjected to chemical or physical treatment in order to change their electrochemical, sorption, adhesive and other characteristics.

Gueccia et al., used diffusion dialysis for the isolation of iron and zinc ions from highly concentrated etching solutions [25]. The studies were carried out using Fumasep FAD anion exchange membranes. Tests performed with membranes have shown high acid recovery efficiencies, indicating a fundamental and synergistic effect of the effect of iron on HCl recovery.

Zimmekman et al., provided an up-to-date review of research on electrodialysis in hydrometallurgical processes, namely, the possibility of separating components and salts using ion-exchange membranes [26].

In a study by some authors [27], the selective extraction of Zn and Fe from spent pickling solutions using a combination of anion exchange and membrane electrolysis methods was previously studied. The experiments were devoted to the anion-exchange separation of the components of the initial solution and the cathodic deposition of iron at various pH values, temperatures and cathode materials using the potentiodynamic test method. It has been found that direct anion exchange with a strong base resin makes it possible to separate the main components (Fe and Zn) of the initial solution loaded into the column at a moderate flow rate.

Dubrawski et al., described the research on the application of electrodialysis for the treatment of industrial copper and zinc electrolytes [28]. The authors have successfully tested three types of ACM anion exchange membranes, PC Acid 60 and PC Acid 100, in combination with a CMS cation exchange membrane.

Badenhorst et al., studied the possibility of using electrolysis to recover iron from spent leaching solutions using membranes [29]. The authors compared the process without the use of a membrane, as well as with porous terylene and newly synthesized anion exchange membranes. Indicators such as current efficiency, specific energy consumption and production of sulfuric acid using own production were studied. According to the research results, it was found that when using new anion-exchange membranes, the optimal concentration of iron is 40 g/dm³, providing high efficiency (99%) and reducing specific energy consumption.

Thus, the electrochemical method of zinc solutions purification from iron, with the associated separation of a number of metal impurities into sufficiently concentrated products, should be considered the most rational [26,29].

The electrochemical method of cleaning zinc solutions from iron, with the associated separation of a number of metal impurities into sufficiently concentrated products,

should be considered the most rational. The electrochemical method is environmentally friendly [30], does not require the use of any additional reagents and gases, as well as the use of a wide variety of technological devices.

The aim of these studies is clarification of the parameters of the purification process of industrial sulfate zinc solutions with a high content of impurities using a membrane electrolyzer.

2. Materials and Methods

For the experiment, a productive solution was taken, obtained by leaching low-grade zinc concentrates at the Hydropolymet pilot (Engineering Dobersek Company, Germany) plant of Kazzinc LLP (Republic of Kazakhstan). The chemical composition of the solution is presented in Table 1. According to the analysis, the solution contained 17.58 g/dm³ Fe(III) and 17.99 g/dm³ Fe(II). To determine the chemical composition, an ICP-MS 7500cx inductively coupled plasma mass spectrometer from Agilent technologies (USA, Santa Clara, CA, USA) was used.

Table 1. Chemical composition of the pregnant leaching solution.

Element	Zn	Fe	Cu	Ni	Co	As	Cd	In
Content, %	10.19	3.57	0.243	0.0013	0.00063	0.003301	0.0553	0.000311

The change in the concentrations of iron (II) and (III) during the experiment was controlled by complexometric titration with sulfosalicylic acid, determining the content of total iron in the form of Fe(III), and the presence of Fe(II)—by the difference in concentrations [31].

The experiment was carried out in two stages to select the most efficient scheme for cleaning the solution from iron impurities. Figure 1 shows the scheme of the experiment.

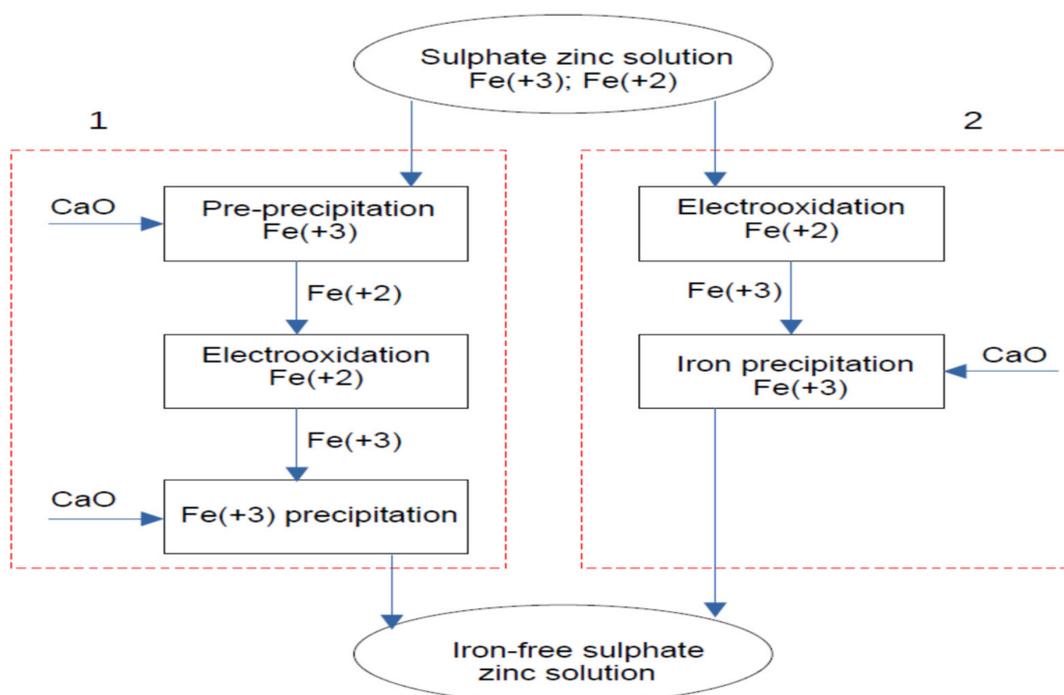


Figure 1. Scheme of the experiment.

The electrooxidation of Fe(II) to Fe(III) was carried out in an electrolytic cell with anion-exchange membranes separating the cathode and anode spaces. The scheme and general view of the laboratory setup are shown in Figure 2a,b.

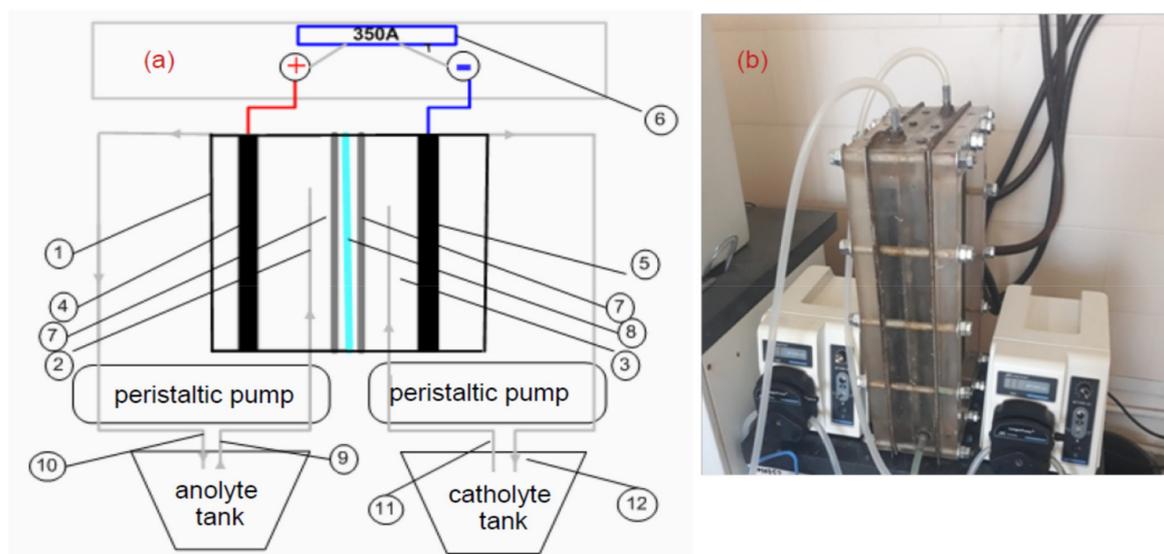


Figure 2. Scheme (a) and general view of the laboratory (b) installation of the membrane. Electrolyzer: 1—cell body; 2—cathode chamber; 3—anode chamber; 4—anode (lead + 1 % silver); 5—cathode (steel plate); 6—power supply; 7—perforated partitions for fixing the membrane; 8—anion-exchange membrane; 9—branch pipe for introducing the solution into the anode chamber; 10—branch pipe for removing the solution from the anode chamber; 11—branch pipe for introducing the solution into the cathode chamber; 12—branch pipe for removing the solution from the cathode chamber.

The studies were carried out in a two-chamber electrolyzer. The electrolyzer is made of plexiglas, all fixing connections are made of stainless steel to prevent corrosion, as shown in Figure 2b. Main operational properties of anion exchange membrane MA-41 TU 2255-062-05761695-2009 (manufactured by Shchekinoazot Innovative Enterprise LLC):

- tensile strength, MPa	17
- size change along the length during swelling, %	6
- surface electrical resistance, Ohm·cm ²	13.2
- transfer number, shares	0.94
- operating temperature, °C	10–50

Since the membrane is produced by the manufacturer only in Cl-form, its preliminary preparation was necessary, which consisted in soaking the membrane for 48 h in a solution containing 60 g/dm³ of H₂SO₄ and 50 g/dm³ of (NH₄)₂S₂O₈. After completion of the process of conversion to SO₄-form, the membrane was ready for installation in the flow electrolyzer. The anode in the flow cell was a platinized titanium plate, and the cathode was a steel plate. The working surface of each electrode was 210 mm × 360 mm = 0.0756 m². To power the electrolytic cell with direct current, an IVT-ZY-500A-12V rectifier unit was used, providing current rectification up to 500 A. According to previous laboratory studies, the optimal current density for efficient iron oxidation was 300–350 A/m². Based on this, the current load during the period of testing on real solutions was 25 A.

Solutions are fed into the electrolytic cell from intermediate tanks using a peristaltic pump through tubes made of acid-resistant material. Solutions continuously circulate between the electrolyzer and intermediate tanks. The solution feed rate to the electrolyzer is constant—60 dm³/min.

Precipitation of iron (presumably in the form of Fe(OH)₃) was carried out in a thermostatically controlled reactor of the LR-2.ST type shown in Figure 3a. calculated stoichiometric amount of lime. The lime slurry was fed into the reactor gradually over 2 h, simultaneously controlling the pH of the solution and taking samples for the content of Fe(III) in the solution. After reaching the set pH value, the pulp was kept under constant

stirring for 1 h of sedimentation. For filtration of ferruginous pulps, a druk-filter was used, shown in Figure 3b.



Figure 3. General view of the LR-2.ST type reactor (a) and the druk-filter (b).

The Course of the Experiment

First type of the experiment with preliminary precipitation of Fe(III).

After preliminary precipitation of Fe(III) hydroxide compounds, the pulp was filtered on the druk-filter at a pressure of 4–5 atm, the resulting solutions were sent for electrooxidation in the anode chamber of the electrolyzer, followed by precipitation of all iron by neutralization with lime (the second stage of precipitation).

The electrooxidation of iron in the solution obtained after the first stage of deposition (the content of Fe(III) 3.19 g/dm³, total iron 11.2 g/dm³) was carried out in the anode chamber of a flow electrolyzer at the current density of 350 A/m² and a circulation rate 2 dm³/h.

Second type of the experiment without preliminary deposition of Fe(III).

The cathode chamber was filled with sulfuric acid (catholyte), the concentration of which was 10 g/dm³, and the anode chamber was filled with the initial solution of the composition g/dm³: 123.8—zinc; 25–30—iron; 2–3—copper; 0.02—nickel. When an electric current is applied to the anode, ferrous iron is oxidized to ferric iron, in addition, the oxidation process takes place due to oxygen, which is released at the anode. Sulfate ions moved through the membrane from the cathode chamber to the anode chamber. As a result of the reaction of ferrous sulfate, sulfuric acid and oxygen, ferric sulfate was formed. Consequently, the divalent form of iron in ionic and molecular form is converted into the trivalent form of iron according to the following reactions (1)–(3):



3. Results

3.1. Stage 1 of the Experiment

Preliminary precipitation of Fe(III) with lime. The final content of Fe(III) in the solution after the operation of preliminary precipitation by neutralization with lime to pH 3.2 was 3.19 g/dm³. The pulps obtained as a result of neutralization of the initial working solution were distinguished by an extremely low filtration rate even when the pressure in the druk-

filter was increased to 5 atm, which is associated with the presence of a significant amount of Fe(II) ions in the solution and, as a result, the formation of complex hydrocompounds of ferrous iron, in particular, basic salts, characterized by extreme dispersity and a tendency to form amorphous difficult-to-filter phases [32]. Figure 4 shows the dependence of the content of Fe(III) in the solution on the pH of the medium at preliminary precipitation of Fe(III) with lime. The dependence of the content of Fe(III) in solution on pH during neutralization with lime is close to linear, the final pH value in the experiments, equal to 3.2, is due to the possibility of precipitation of hydrated zinc compounds and impurities on the surface of CaO particles, an increase in the consumption of the latter, dilution of the solution formed by the neutralization reaction water and possible deterioration of filterability of pulps.

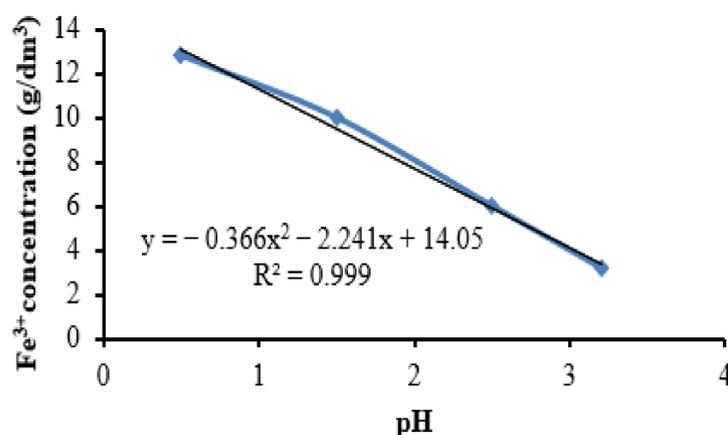


Figure 4. Dependence of Fe(III) content in solution on the pH of the solution.

Subsequent electrodeposition. Under the above conditions, changing the content of ferric iron in solution during electrooxidation in the anode chamber is shown in Figure 5. The content of sulfuric acid in the solution increases, which is associated with the occurrence of an electrochemical reaction of oxygen evolution at the anode as a result of water decomposition. The rate of iron oxidation was about 2.7–3.1 g/dm³ per hour, and the time required for complete oxidation of iron exceeded 3 h.

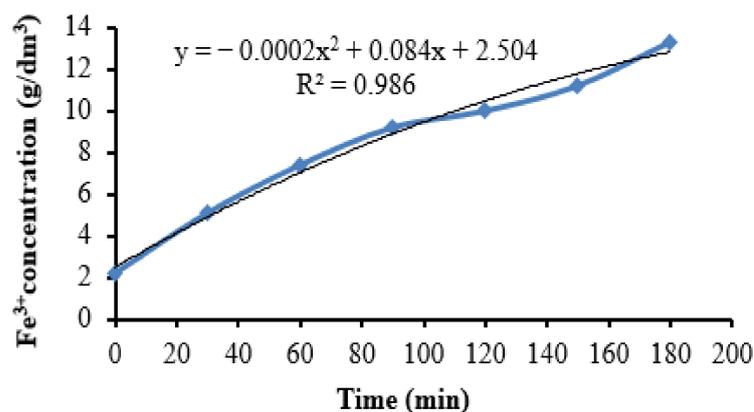


Figure 5. Change in the concentration of Fe(III) during electrooxidation in a flow cell.

The concentration of total iron during electrooxidation practically does not change (Figure 6), which indicates the absence of the possibility of the formation of poorly soluble iron compounds during the process.

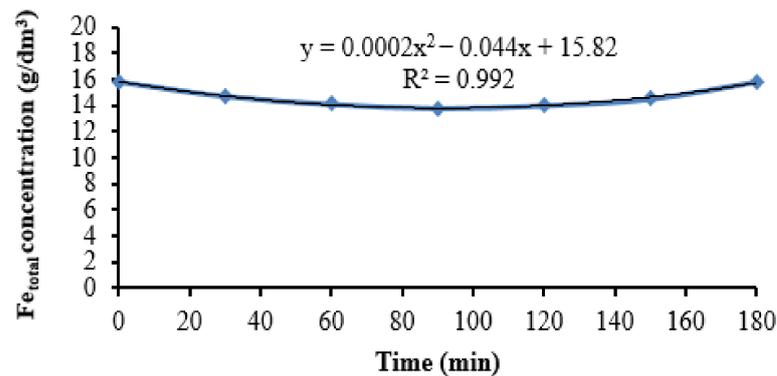


Figure 6. Change in the concentration of Fe_{total} during electrooxidation in the flow cell.

During the electrooxidation of iron in the flow cell, the content of sulfuric acid in the solution increases (Figure 7), which is associated with the occurrence of an electrochemical reaction of oxygen evolution at the anode as a result of water decomposition. The determination of H₂SO₄ was carried out by direct titration with a standard alkali solution. The pH at the equivalence point is 7. Methyl orange [33] was used as an indicator.

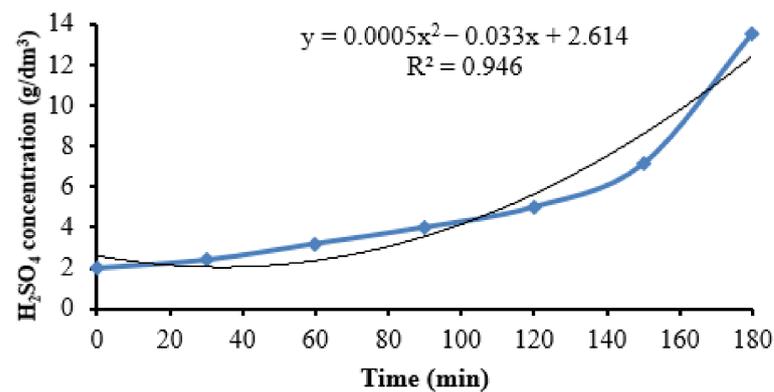


Figure 7. Change in H₂SO₄ concentration during the electrooxidation in the flow cell.

The change in voltage across the cell is shown in Figure 8. The voltage across the cell stabilizes at 6–6.5 V within 40–50 min after the start of the process, which is associated with the operation of the cell without circulation of the solution during this period of time.

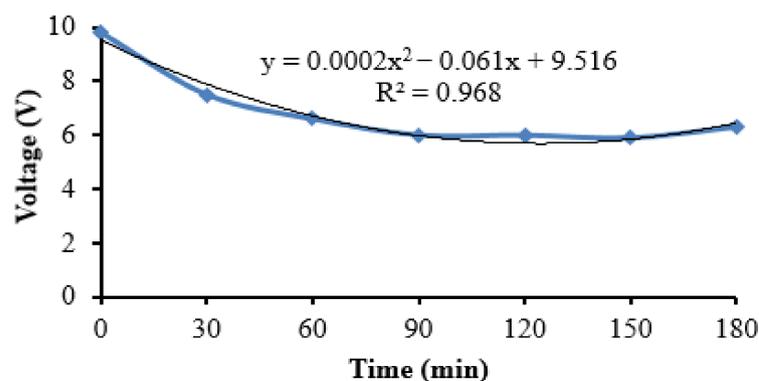


Figure 8. Change in voltage on the cell.

Due to the poor filterability of the pulps of the first stage of iron precipitation, attempts were made to carry out the electrooxidation of iron directly in the real Hydropolymet solution, bypassing the stage of preliminary precipitation of Fe(III) hydroxide compounds.

According to [32], in the presence of Fe(II) ions, X-ray amorphous $\text{Fe}(\text{OH})_2$ aggregates are formed, the size of which does not exceed $5\ \mu\text{m}$, while iron sulfates form well-crystallized FeOOH (ferric iron oxyhydroxides) three modifications, with a certain particle morphology. The average size of the formed crystals depends on the completeness of the oxidation process, therefore, affects the filterability of the resulting precipitate.

3.2. Stage 2 of the Experiment

In the second series of experiments, a real solution was used as the anolyte, Hydropoly-met obtained by leaching low-grade zinc concentrates. The process of electrooxidation of the working solution was carried out in the anode chamber of the flow cell at a current density of $350\ \text{A}/\text{m}^2$ and a circulation rate of $2\ \text{dm}^3/\text{h}$. The change in Fe(III) concentration during electrooxidation is shown in Figure 9.

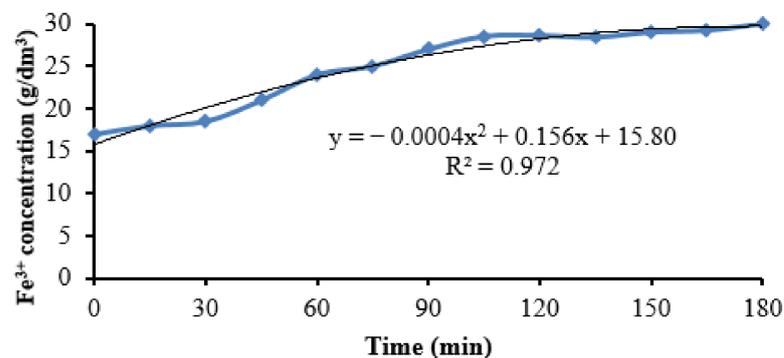


Figure 9. Fe(III) concentration change during electrooxidation in the flow electrolyzer (solution without preliminary iron precipitation).

Figure 8 shows that almost complete oxidation of iron occurs within 90–100 min from the start of the process, which indicates the efficiency of using the working solution as an anolyte without preliminary precipitation of Fe(III). Accordingly, there is a change in the content of total iron in the solution. The change in the acidity of the anolyte (Figure 10) is more noticeable than in the experiments with preliminary precipitation of iron, which may be due to the excessive duration of the experiment, i.e., operation of the electrolytic cell at almost complete oxidation of Fe(II) to Fe(III).

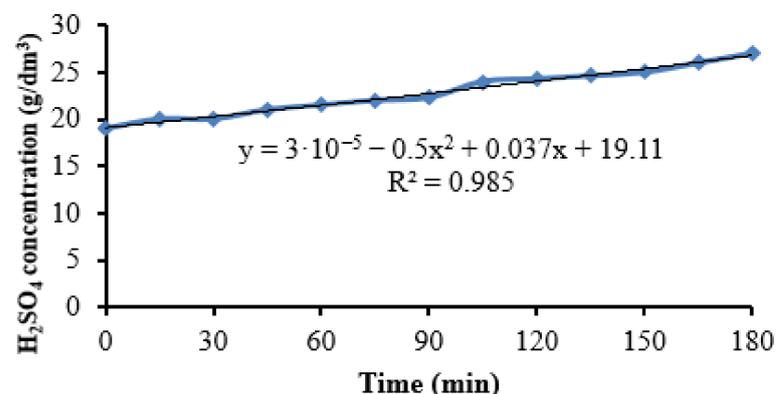


Figure 10. Change in the concentration of H_2SO_4 during electrooxidation in the flow electrolyzer (solution without preliminary precipitation of iron).

The increase in the voltage on the bath (Figure 11) after 90–100 min is associated with the completion of the process of anodic oxidation of iron and the increase in the proportion of the water decomposition reaction in the solution with increasing acidity.

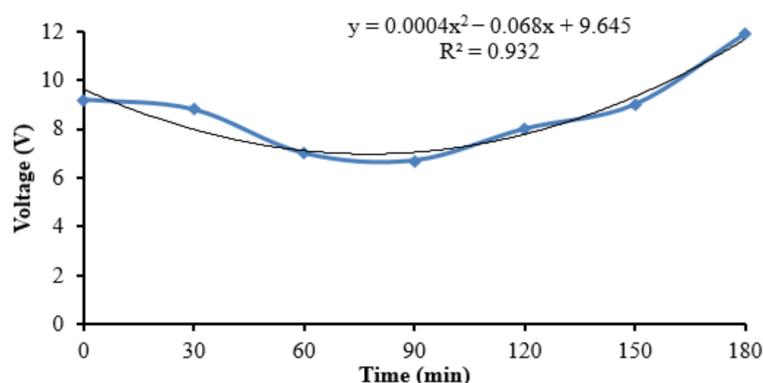


Figure 11. Changing the voltage on the cell.

Precipitation of Fe(III) hydrated compounds after direct electrooxidation of the working solution was carried out according to the same procedure as two-stage precipitation with intermediate electrooxidation of iron.

The dependence of the content of Fe(III) in the solution on pH during the precipitation of iron from solutions after electrooxidation of real working solutions of Hydropolymet is shown in Figure 12. It is obvious that the neutralization of solutions to pH 3.5 is sufficient for the quantitative precipitation of iron in the form of hydrated compounds.

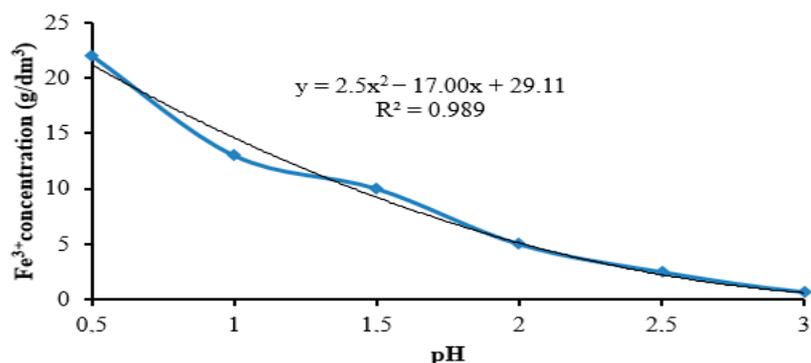


Figure 12. Dependence of Fe(III) content in solution on the pH.

Precipitate obtained after Fe(III) precipitation from direct electrooxidation solutions (Figure 13) was characterized by good filterability (filtration rate 1.5–2 m³/m²·h) and greater compactness.



Figure 13. Precipitate obtained after Fe(III) precipitation from direct electrooxidation solutions.

Thus, direct electrooxidation of sulfate zinc solutions obtained by leaching low-quality zinc concentrates in the anode chamber of the flow electrolyzer provides good filterability of precipitates after hydrolytic precipitation, since this solution does not contain Fe(II) ions,

the presence of which leads to significant difficulties in the operations of separating solid and liquid phases. The average indicators for conducting the electrooxidation process are shown in Table 2.

Table 2. Average indicators for carrying out the electrooxidation process.

Current Density, A/m ²	Electrolyte Feeding Rate, dm ³ /min	The Initial Composition of the Electrolyte Fe ²⁺ , g/dm ³	Initial pH Value of the Electrolyte	Experiment Duration, min
25	60	17.208	0.5	180

The obtained experimental values of the concentration of iron in the solution are shown in Figure 14.

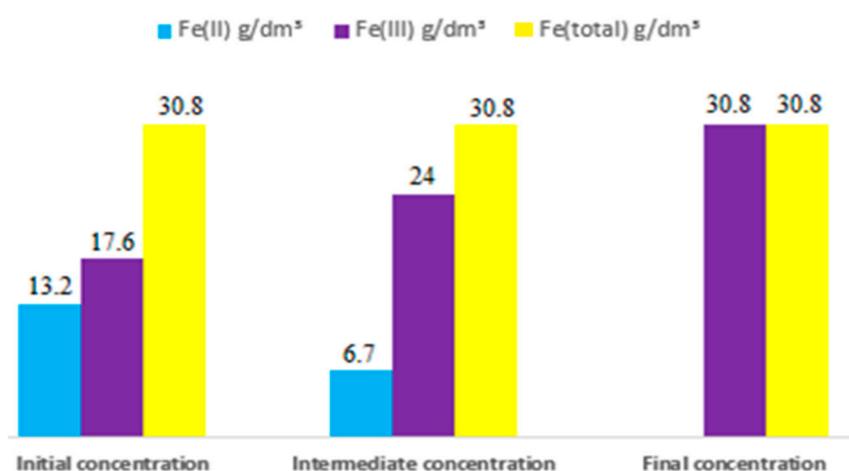


Figure 14. The concentration of iron in the solution after oxidation in the electrolyzer.

As a result of laboratory studies using the membrane electrolyzer, ferrous iron in sulfate zinc solutions was completely converted into ferric iron. Further tests will be carried out to get a complete purification from the remaining impurities.

The next stage of the study is to determine the conditions and parameters for the removal of electropositive impurities (copper cations, in particular) in the cathode chamber of the electrolytic cell by electrocarburizing.

4. Conclusions

It has been established for the first time that during the preliminary precipitation of Fe(III) ions from real sulfate solutions, difficult-to-filter pulps are obtained, and direct electrooxidation of sulfate zinc solutions in the anode chamber of the flow membrane electrolyzer provides good filterability of precipitation after hydrolytic precipitation of iron, since there are no ions in this solution. Fe(II), the presence of which leads to significant difficulties in the operations of separating the solid and liquid phases. This makes it possible to exclude the thickening operation from the technological scheme. The degree of oxidation of iron during the test period was 99.8–99.9%. The residual concentration of iron after precipitation from solutions obtained after electrochemical oxidation in the form of oxide and hydroxide compounds was less than 0.01 g/dm³.

Author Contributions: Conceptualization, L.L., Z.O. and N.K.; Methodology, S.M. and O.A.; Software, L.L.; Validation, L.L., Z.O., G.D., S.M. and O.A.; Formal analysis, L.L., Z.O., G.D. and O.A.; Investigation, L.L., Z.O. and N.K.; Resources, L.L., G.D. and O.A.; Data curation, L.L., Z.O., N.K. and O.A.; Writing—original draft preparation, L.L., Z.O., N.K., S.M. and O.A.; Writing—review and editing, L.L., Z.O., N.K., S.M., G.D. and O.A.; Visualization, L.L., Z.O. and G.D. All authors have read and agreed to the published version of the manuscript.

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